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Direct Conversion of Chemically De-Ashed Coal in Fuel Cells (II)

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We review the technical challenges associated with the production and use of various coal chars in a direct carbon conversion fuel cell. Existing chemical and physical de-ashing processes remove material below levels impacting performance at minimal cost. At equilibrium, sulfur entrained is rejected from the melt as COS in the offgas.

A carbon fuel cell reacts elemental carbon and atmospheric oxygen in a molten carbonate electrolyte according to the reaction $C + O_2 = CO_2$ ($E^\circ = 1.02$ V, 750° C). Fuel cells with anodes of atomically disordered “turbostratic” carbon have been operated at 0.8 V and 1 kA/m² with essentially pure CO₂ product gas—indicating potential for conversion of fossil fuel chars at 80% of the HHV of carbon.¹

The use of coal or petroleum-coke chars in such fuel cells may give rise to problems of electrolyte fouling resulting from entrainment of inorganic material (“ash” and sulfur) with the anode. Weaver found that ash at levels up to 10% had no perceptible effect on cell voltages.² For a typical salt loading ($W_{el} \sim 2.3$ g/cm²), current density ($i = 0.1$ A/cm²), and mass fraction of ash f , the time T_c to reach this critical concentration ($f_c = 0.10$) is given by:

$$T_c = \frac{f_c n F W_{el}}{i M_c f} \quad (1)$$

M_c is the atomic weight of carbon and F is the Faraday constant. This criterion suggests a useful life of the melt of T_c (days) $\sim 0.86/f$. Thus for the mechanically cleaned coal granules with 0.17-1 % ash, the critical time T_c is 506 to 86 days. For the solvent-extracted sources of fuel having < 0.05% ash, equation (1) leads to a time to exhaust the melt approaching 5 years—roughly the life expected for any high temperature cell.

We examined the energy balances and costs associated with deep chemical cleaning of bituminous coal by several pilot processes that now reduce ash levels below 0.2% at costs of \$3/GJ. The costs and residual ash are given in Table 1.

Table 4. Costs of extracting the carbon anode from coal

Process/ Developer	Yield, %	Ash, %	S, %	Fuel Cost
U. Ky. Mechanical separation ³	90	<1	1-2	\$60/ton
Bayer leaching; UCC Energy, Ltd. Pty. ⁴	--	0.17-0.27	0.4 2	\$3.0-3.3 /GJ
NEDO process ⁵	60%	<0.02	--	~ \$2/GJ
Solvent, U. Kentucky ⁶	40-70	0.01-0.06	0.5	--
WVU-NMP solvent ⁷	40-50	0.04-0.3	1.0	\$140/ton ^b ,

^b Calcined extract.

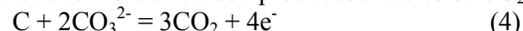
Cleaned coal will retain a few percent of bound sulfur and some residual pyrite. Thermodynamic equilibrium calculations (FACT 2.1⁸) indicate that sulfur is stable in the C/CO₂/Na₂CO₃ system at 750 °C only as sulfide ion in the condensed phase in equilibrium with gaseous COS



The equilibrium relation is:

$$[COS]/[CO_2]^2 = K_{750^\circ C} = 0.0225 \text{ atm}^{-1} \quad (3)$$

Reaction of one mole of carbon produces 3 moles of CO₂:



At equilibrium, 0.0675 moles of sulfur may be removed as COS per mole of carbon reacted, corresponding to the removal of all sulfur up to a weight percent of 18%-wt.

Were the sulfide to migrate to the cathode, it would be oxidized to the sulfate ion. Solution of the flux equation for the system (Na,K)₂CO₃, (Na,K)₂S, (Na,K)₂SO₄ allows us to estimate the rate of transport of sulfide and the steady state concentration profiles of sulfide and sulfate ions within the separator. Regardless of the fate and transport of sulfur entrained with coal, the corrosiveness of reduced sulfur for most metals severely limits materials of construction and current collection.

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